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Oxidative and thermal stabilities of genetically modified high oleic sunflower oil

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Abstract

The oxidative and thermal stabilities of genetically modified high oleic sunflower oil (87% oleic acid) were compared with those of regular sunflower (17% oleic acid), soybean, corn, and peanut oils during storage at 55 °C and simulated deep fat frying at 185 °C. Oxidative stability was evaluated by measuring the oxygen content and volatile compounds in the sample bottle headspace and peroxide value. The coefficient variations (CVs) for volatile compound, headspace oxygen, and peroxide value analyses were 2.02%, 1.41%, and 3.18%, respectively. The oxidative stability of high oleic sunflower oil was greater than those of regular sunflower and soybean oil ($P < 0.05$) and as good as those of corn and peanut oils ($P > 0.05$). The thermal stabilities of oils during deep fat frying were evaluated by measuring the infrared absorption at 2.9 μm and conjugated diene content. The CV of conjugated diene content was 1.07%. Infrared and conjugated diene results showed that the high oleic sunflower oil had greater thermal stability than had regular sunflower, soybean, corn, and peanut oils ($P < 0.05$). The genetically modified high oleic sunflower oil, with 5.5% linoleic acid, had better oxidative and thermal stabilities than had the regular sunflower oil with 71.6% linoleic acid.

Keywords: High oleic sunflower oil; Oxidation; Thermal stability; Headspace analysis; Conjugated diene

1. Introduction

Vegetable oils undergo extensive oxidative deterioration due during storage, marketing, or deep fat-frying. Hydroperoxide, which is the major oxidation product, decomposes to secondary products, such as esters, aldehydes, alcohols, ketones, lactones and hydrocarbons. These secondary products adversely affect flavour, aroma, taste, nutritional value and overall quality of foods. Additionally, certain oxidation products are potentially toxic at relatively low concentrations (Min & Boff, 2001; Nawar, 1996). Oil oxidation can be determined by oxygen depletion, peroxide value, volatile compounds, conjugated diene content and flavour score (Dunlap, White, Pollak, & Brumm, 1995; Hahm & Min, 1995; Min & Schweizer, 1983).

The composition of oleic, linoleic and linolenic acids in oil has been an affect the oxidative stability (Min & Boff, 2001; Nawar, 1996). Sunflower oil has approximately 70% linoleic acid (Meydani et al., 1991) and is highly susceptible to lipid oxidation (Jeleń, Obuchowska, Zawirska-Wajtasiak, & Wasowicz, 2000). Heating speeds up the oxidative reaction, which is a major concern for deep fat-frying operations (Muik, Lendl, Molina-Díaz, & Ayora-Canada, 2005). Ashton, Best, and Ball (2001) reported that high oleic sunflower oil may decrease the risk of coronary heart disease by decreasing low density lipoprotein (LDL) cholesterol susceptibility to oxidation. Genetic modification of sunflower oil, to decrease linoleic acid and increase oleic acid, could increase the oxidative stability during storage and deep fat-frying, as well as improve the health benefits. However, there is not much information on the oxidative stabilities of modified vegetable oils, especially sunflower oil, available. The objective of this study is to compare the oxidative stability and the thermal deep

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fat-frying stability of genetically modified high oleic sunflower oil with those of regular sunflower, soybean, corn and peanut oils during storage at 55 °C and simulated deep fat frying at 185 °C.

2. Materials and methods

2.1. Experimental oils

High oleic acid sunflower oil and regular sunflower oil were from SVO International, Cleveland, OH. Soybean oil, corn oil and peanut oil were from Capital City Products, Columbus, OH. To maintain the freshness of the oils, all oils were stored frozen at −20 °F from the time they were received until they were to be used.

2.2. Fatty acid composition determination

The oils were derivatized to fatty acid methyl esters in 5 ml vial. A 10 mg aliquot was transferred into a vial and 0.6 ml of sodium methoxide was then added. Each of the vials was capped and heated at 60 °C for 60 min. Following the heating, 0.6 ml of saturated NaCl solution and 0.4 ml of petroleum ether were added to the vial. Oil samples were methylated in duplicate.

One microlitre of the fatty acid methyl esters in the petroleum ether was injected into a Hewlett-Packard 5890 gas chromatograph equipped with a flame-ionization detector. The temperatures of the oven, injector, and detector were 185, 200 and 250 °C, respectively.

2.3. Sample preparation for oxidative stability determination

Fifteen grams of oil were transferred to a 30 ml serum bottle. The sample bottle was sealed (air-tight) with a Teflon-coated rubber septum and aluminium cap. The samples were stored in a forced-draft air oven at 55 °C and evaluated in triplicate every 24 h for 5 days (Mistry & Min, 1987).

2.4. Headspace oxygen and volatile compound determination

The oxygen disappearance and volatile compound formation in the headspace of the samples was measured by gas chromatography (Mistry & Min, 1987). Each sample was allowed to equilibrate to ambient temperature for 1 h after the sample was removed from the oven. The headspace oxygen was determined by directly injecting 1 ml of headspace air into the gas chromatograph equipped with molecular sieve 13× (Supelco, Beelfonte, PA) and a thermal conductivity detector, and electronic integrator.

The amount of volatile compounds formed during storage was measured by injecting 1 ml of headspace air directly into a Hewlett-Packard 5880 gas chromatograph equipped with an electronic integrator and flame ionization detector. The column was stainless steel (3.05 m × 0.32 cm) packed with 80/100 mesh Tenax GC coated with 10% polymetaphenoxylene (Supelco Co., Bellefonte, PA). The injector, column and detector temperatures were 200, 120 and 250 °C, respectively. The nitrogen carrier gas flow rate was 24 ml/min. The gas chromatograph was calibrated using 1% ethyl hexanoate in ether as an external standard.

2.5. Peroxide value

The peroxide values of the five oils were determined in duplicate by the American Oil Chemists' Society (AOCS) Official Method Cd 8-53 (1980).

2.6. Deep fat frying process

The deep frying method used is similar to the deep fat frying method used by Andrikopoulos, Dedoussis, Falirea, Kalogeropoulos, and Hatzinikola (2002). In this study, cotton balls were used instead of potatoes, frying time was 3 min instead of 10 min, a frying temperature of 185 °C, and total frying time was 24 h for 4 days at 6 h/day.

Oil (2300 ml) was heated to 185 ± 5 °C in a Dazey Chef deep fat-fryer (Model DCP-35) equipped with a temperature control probe. The fryer was made of die cast aluminium with Dazite non-stick coating, and had a capacity of 3.5 quarts, and used 1400 W of electricity. One hour was allowed for the oil to reach and stabilize at frying temperature. Ten cotton balls (Q-tips, Greenwich, CT), each containing 75% by weight of distilled, demineralized water (0.445 ± 0.025 g cotton ball containing 1.50 ± 0.02 g water) were fried in the oil for 3 min and then removed. It was necessary to squeeze as much of the absorbed oil as possible from the cotton balls before discarding them in order to minimize oil loss. A fresh set of moist cotton balls was fried every 30 min for a period of 6 h, as in the method used by Krishnamurthy, Kawada, and Chang (1965). The oil was covered and then allowed to cool and stand overnight. Before resuming the frying on the following day, 400 ml of fresh oil were added to the fryer to replenish the oil lost by absorption of the cotton balls. This frying was repeated for a total of 24 h for 4 days at 6 h per day.

2.7. Infrared analysis

The infrared spectrum of oil was determined in duplicate, using a Beckman AccuLab 2 Infrared Spectrophotometer. A sample size of 15 mg of oil was chosen to obtain the best spectrum possible and was applied to a sodium chloride cell for scanning.

2.8. Conjugated diene content determination

The five oils were analyzed in duplicate for conjugated diene according to the modified version of the AOCS Official Method Ti 1a-64 (1980). In the modified AOCS method, a sample size of 25.0 mg was diluted to 25.0 ml and no additional dilutions were made. The conjugated

diene content was determined at 233 nm, in duplicate, using a Hitachi Spectrophotometer Model 100 and was then converted to % conjugated dienoic acid.

3. Results and discussion

3.1. Fatty acid compositions of oils

The fatty acid compositions of the high oleic acid sunflower, regular sunflower, soybean, corn, and peanut oils are listed in Table 1. The coefficient of variation (CV) for the fatty acid analysis was 1.41%. Genetically modified high oleic sunflower oil contains 87.4% oleic acid, about 70% more than regular sunflower oil, and 5.45% linoleic acid, which is about 66% less than regular sunflower oil. The fatty acids, which are in a non-radical singlet state, do not directly react with atmospheric oxygen, which is in a radical triplet state (Choe & Min, 2005a). In oxidation reactions, the non-radical fatty acid is converted into a free radical by removing a hydrogen atom before reacting with the radical atmospheric oxygen (Fig. 1). Free radical formation at C8 of oleic acid and C11 of linoleic acid requires 75 kcal/mole and 50 kcal/mole, respectively. The oxidative rates of oleic acid, linoleic acid and linolenic acid are 1:12:25 (Min & Boff, 2001). Therefore, the high oleic acid sunflower oil should have better oxidative stability than the regular sunflower oil with high linoleic acid. Corn oil and peanut oil should have better oxidative stability than regular sunflower oil and soybean oil, based on the linoleic and linolenic acid contents in the oil. However, it should be kept in mind that the oxidative stabilities of the oils are influenced by the amount and type of metals, natural antioxidants, phospholipids, free fatty acids, mono- and

Table 1
Fatty acid compositions (%) of high oleic acid sunflower, regular sunflower, soybean, corn, and peanut oils

Oil	16:0	18:0	18:1	18:2	18:3
High oleic sunflower	4.85	2.34	87.4	5.45	0.0
Regular sunflower	6.74	4.45	17.2	71.6	0.0
Soybean	11.1	3.33	25.6	54.6	5.40
Corn	11.8	1.33	28.2	58.6	0.0
Peanut	12.1	1.51	51.8	34.6	0.0

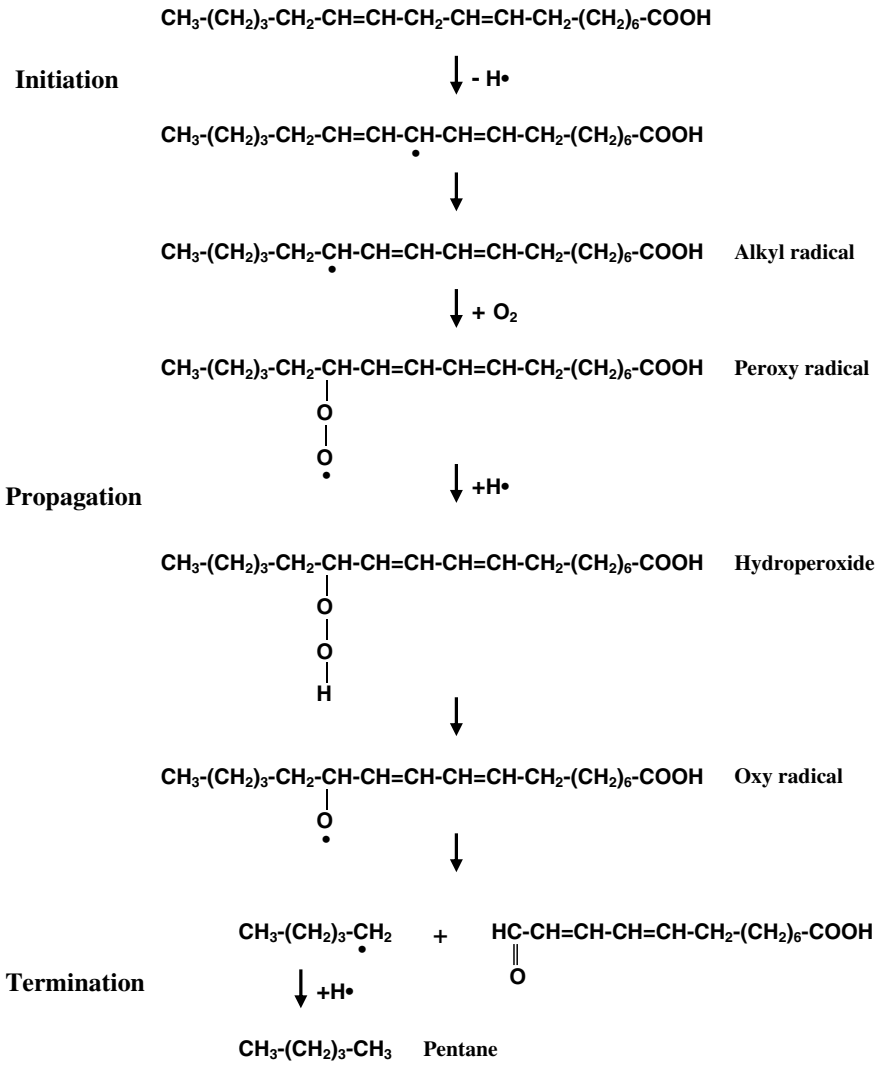

Fig. 1. Chemical mechanism of fatty acid oxidation.

di-glycerides, polymers and the number of double bonds in the oil.

3.2. Oxidative stability evaluation of oils

3.2.1. Headspace oxygen determination

Oxidation rate is independent on oxygen concentration at high levels of oxygen but, when oxygen levels are low, the rate of oxidation is almost proportional to the oxygen concentration (Nawar, 1996). The headspace oxygen content of the oils during storage is shown in Fig. 2. The CV for headspace oxygen was 1.29% (Table 2). The headspace oxygen of high oleic sunflower, regular sunflower, soybean, corn and peanut oils decreased over 5 days. Headspace oxygen depletion is the result of oxygen reacting with the oil sample to form peroxy radicals (Fig. 1). The amount of headspace oxygen depletion indicated that peanut and corn oils were the most stable to oxidation. High oleic sunflower, regular sunflower and soybean oils were least stable to oxidation, though high oleic sunflower oil has a significantly greater stability than regular sunflower oil ($P < 0.05$).

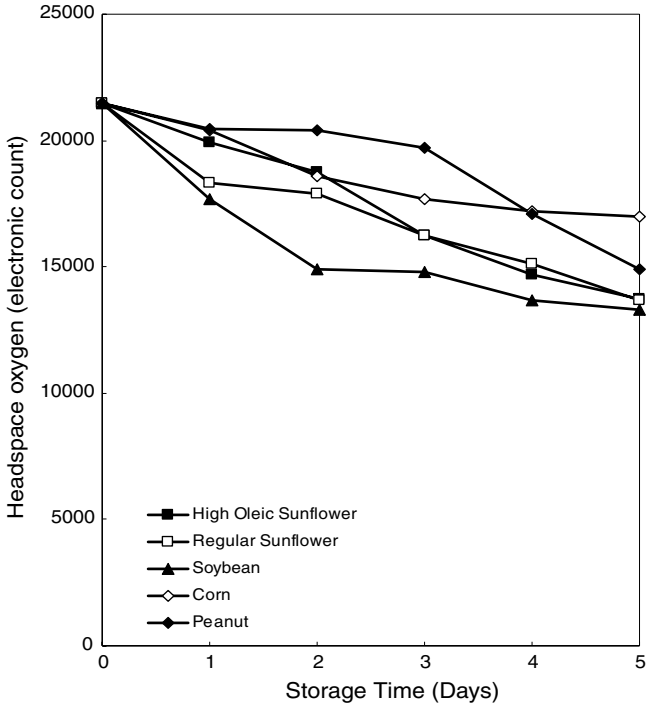

Fig. 2. Headspace oxygen content (electronic count) in oil bottles during 5 days at 55 °C.

Table 2
Coefficients of variations (CV) for the analyses of headspace oxygen uptake, peroxide value and conjugated diene content of soybean oil

Analysis	Oxygen (%)	Peroxide value (meq/kg)	Conjugated diene content (%)	Volatile compounds[a]
1	13.6	6.90	0.503	129.34
2	14.0	7.20	0.510	128.90
3	13.7	7.10	0.513	125.09
4	14.0	7.25	0.514	128.24
5	13.7	7.25	0.515	132.00
6	14.0	7.65	0.519	132.11
Mean	13.8	7.24	0.512	129.28
Standard deviation	0.18	0.23	0.005	2.61
CV (%)	1.29	3.17	0.98	2.02

[a] Volatile compounds (electronic counts).

3.2.2. Peroxide value

Peroxide value is a common method used to measure lipid oxidation, and is suitable for measuring peroxide formation in the early stages of oxidation (Nawar, 1996). The peroxide values of oils during storage are shown in Fig. 3. The CV for peroxide value analysis was 3.17% (Table 2). Peroxide values of the oils increased during storage (Fig. 3). Based on the peroxide values, peanut and corn oils had the greatest oxidative stabilities, followed by high oleic sunflower oil. Regular sunflower and soybean oils were the least stable.

3.2.3. Volatile compounds

The off-flavour of oil is due to the volatile compounds formed during oxidation. Formation of volatile compounds in the oils during storage is shown in Fig. 4. The CV for volatile compound analysis was 2.02% (Table 2). The results from the volatile compound analysis indicate that peanut, corn, and high oleic acid sunflower oils were the most stable to oxidation, followed by regular sunflower oil. Soybean oil was the least stable. The oxidative stability

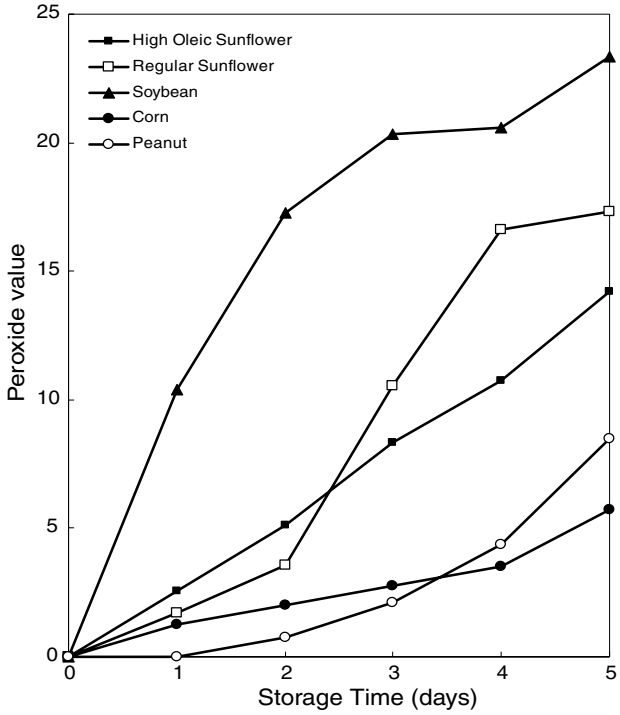

Fig. 3. Peroxide values of oils during 5 days at 55 °C.

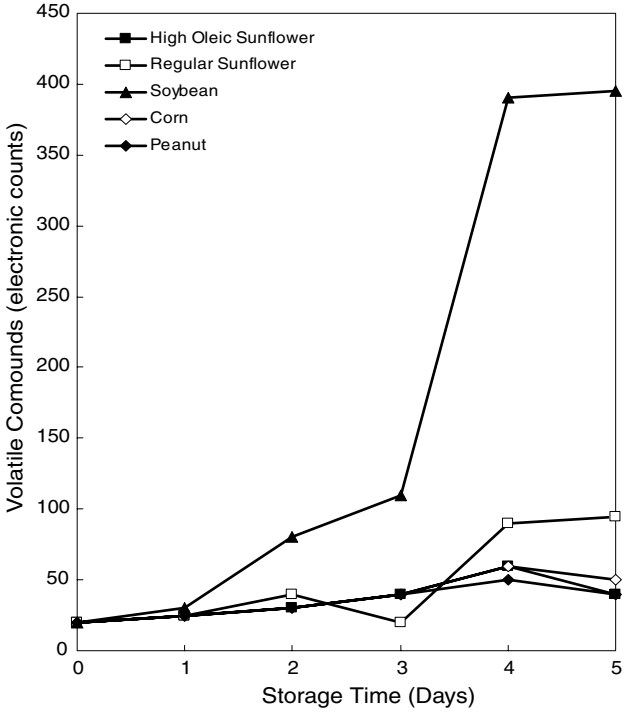

Fig. 4. Headspace volatile compounds of oil bottles during 5 days at 55 °C.

of the high oleic sunflower oil was significantly greater than that of the regular sunflower oil ($P < 0.05$).

3.3. The relationship between headspace oxygen depletion, peroxide value, and volatile compounds

The chemical mechanism of fatty acid oxidation (Fig. 1) explains the headspace oxygen depletion, the formation and decomposition of hydroperoxides and the formation of volatile compounds during lipid oxidation. Headspace oxygen is continuously depleted to form hydroperoxide during storage. Peroxide values decrease with increased storage time, while oxidation and volatile compound formation increase with time. As storage time increases, the formation rate of hydroperoxide becomes less than the decomposition rate, resulting in decreased peroxide values. For this reason peroxide value alone is not an accurate evaluation of quality of oil, especially during the later stages of oil oxidation.

3.4. The relationship between fatty acid composition and oil oxidative stability

Headspace oxygen, peroxide value and volatile compound analyses (Figs. 2–4) showed that corn, peanut, and high oleic sunflower oils have significantly better oxidative stabilities than have the regular sunflower and soybean oils ($P < 0.05$). Table 1 shows that regular sunflower and soybean oils have higher linoleic and linolenic acid contents than have the other oils. These results indicate that oils with high linoleic and linolenic contents have low oxidative stabilities. This is because the oxidation reaction rates of linoleic and linolenic acid are 12 and 25 times greater than that of oleic acid, respectively (Min & Boff, 2001).

3.5. Thermal stability evaluation of oils during deep fat frying infrared analysis

Infrared analysis is becoming an important quality control tool in the food industry and has been used to follow soybean oil deterioration during deep fat frying (Goburdhun, Jhaumeer-Laulloo, & Musruck, 2001). The infrared spectrum of high oleic sunflower, before and after simulated deep fat-frying (24 h at 185 °C), is shown in Fig. 5. An absorption peak at 2.9 μm was observed following frying; however, this peak was not present in fresh oil. The 2.9 μm peak was due to the intermolecular hydrogen bonds of hydroxyl groups in compounds formed during the oxidation of the oils (Min & Boff, 2001; Siverstein, Basseeler, & Morrill, 1981). The relative peak sizes at 2.9 μm for high oleic sunflower oil, corn oil, peanut oil, regular sunflower oil and soybean oil, after deep fat frying for 24 h, were 1:2:2:3:3, respectively (data not shown). The infrared spectra analysis suggests that high oleic acid sunflower oil is more thermally stable than are corn, peanut, regular sunflower or soybean oils.

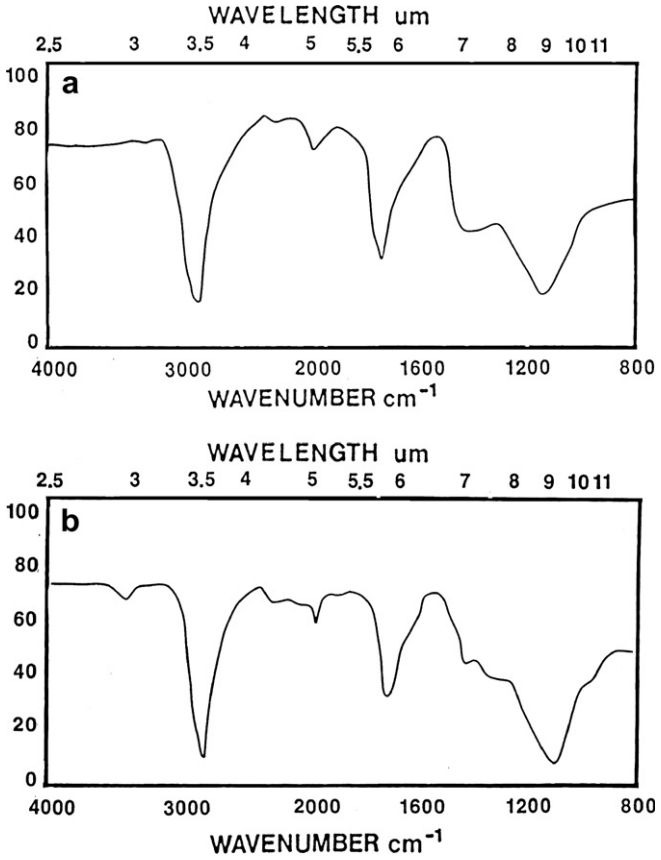

Fig. 5. Infrared spectra of high oleic sunflower oil before (a) and after (b) simulated deep fat frying (24 h at 185 °C).

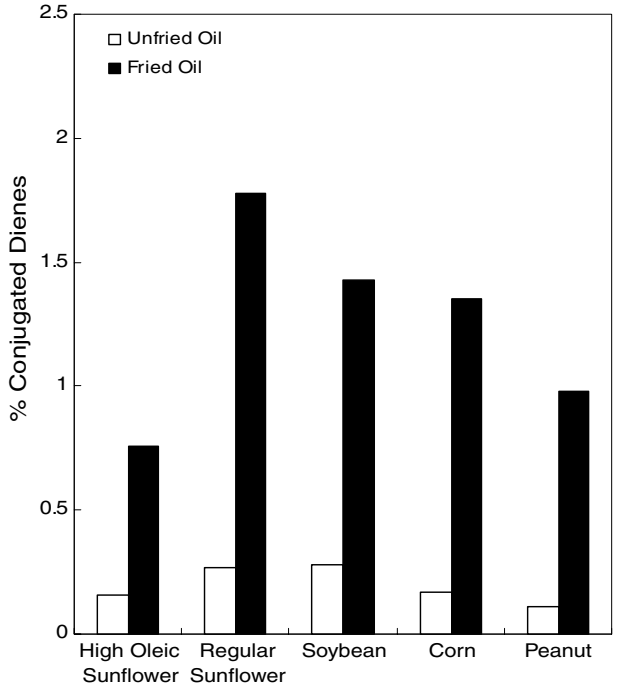

Fig. 6. Conjugated dienes of oils before and after the simulated deep fat-frying at 185 °C for 24 h.

3.6. Conjugated diene content

Conjugated dienes are formed during the oxidation of unsaturated fatty acids, containing two or more double bonds, to achieve a more stable radical (Fig. 1). The initial radical electron at C11 of linoleic acid is delocalized through five carbon systems from C9 to C13 and then forms a stable conjugated diene with a radical at C9 or C13 (Choe & Min, 2005b). The CV for conjugated diene content was 1.07% (Table 2). The diene contents of high oleic sunflower, regular sunflower, soybean, corn and peanut oil were determined before and after simulated deep fat frying (Fig. 6). The result showed that the high oleic acid sunflower oil may be more resistant to thermal deterioration than are the other oils. Edible vegetable oils, low in polyunsaturated fatty acids, have been reported to undergo lower conjugated diene formation at 160 °F (Muik et al., 2005). The formation of conjugated diene during frying was proportional to the linoleic acid content of the oil (Table 1). The results of the conjugated diene analysis indicate high oleic sunflower oil as the most thermally stable oil.

4. Conclusion

Genetically modified high oleic sunflower oil had a higher oxidative stability during storage than had regular sunflower oil. Similarly, the thermal stability evaluation results indicate a greater stability for modified high oleic sunflower oil than for regular sunflower oil. The oxidative and thermal stabilities of edible oils appear to be related to linoleic and linolenic contents, decreased linoleic and linolenic contents result in increased oil stability.

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